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A STATISTICAL EXAMINATION OF THE EFFECT OF COMPOSITION  
ON THE FREEZING POINTS OF HYDRO-CARBON MIXTURES(U)

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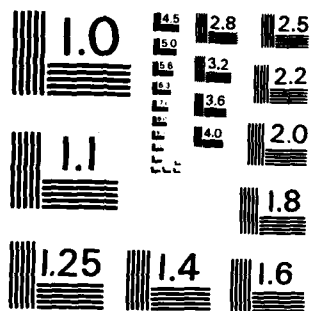
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NRL Report 8802

# A Statistical Examination of the Effect of Composition on the Freezing Points of Hydrocarbon Mixtures

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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER NRL Report 8692	2. GOVT ACCESSION NO. AD-A131000	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) A STATISTICAL EXAMINATION OF THE EFFECT OF COMPOSITION ON THE FREEZING POINTS OF HYDRO- CARBON MIXTURES	5. TYPE OF REPORT & PERIOD COVERED Interim report on one phase of an NRL problem	
7. AUTHOR(s) W. A. Affens, R. N. Hazlett, and D. E. Smith*	6. PERFORMING ORG. REPORT NUMBER	
9. PERFORMING ORGANIZATION NAME AND ADDRESS Naval Research Laboratory Washington, DC 20375	8. CONTRACT OR GRANT NUMBER(s)	
11. CONTROLLING OFFICE NAME AND ADDRESS Naval Air Propulsion Center Trenton, NJ 08628	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 6276N ZF65371006 61-0085-0-3	
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)	12. REPORT DATE July 21, 1983	
	13. NUMBER OF PAGES 15	
	15. SECURITY CLASS. (of this report) Unclassified	
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE	
16. DISTRIBUTION STATEMENT (of this Report)  Approved for public release; distribution unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES  *Desmatic, Inc., State College, PA 16801		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Freezing point Hydrocarbon fuels n-Alkane mixtures Jet fuels		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) A series of three statistically designed experiments was run to study the effect of composition on the freezing point of model hydrocarbon fuels. For each experiment, regression equations were derived to describe the effect of composition on freezing point for various mixtures of n-alkanes and other hydrocarbons. These experiments showed that the higher n-alkanes and the interactions among them play an important role in freezing point. The n-alkanes C-16, C-15, and C-14 (in that order) had a strong positive effect (raised the freezing point). The n-alkanes C-12 and C-13 also had strong effects, with C-12 and C-13 in combination showing strong negative effects. However, the magnitude (Continued)		

20 ABSTRACT (Continued)

and direction (positive or negative) of the C-12 and C-13 effects (individually and in combination) were greatly dependent on the concentration of C-16. In general C-12 and C-13 individually had a positive effect when the C-16 mole fraction was small (less than 1.67 mol-%) but a negative effect in the presence of higher C-16 concentrations. The n-alkanes C-10 and C-11 had negligible effects. These behaviors were consistent with the results of previous NRL studies.

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# A STATISTICAL EXAMINATION OF THE EFFECT OF COMPOSITION ON THE FREEZING POINTS OF HYDROCARBON MIXTURES

## INTRODUCTION

Since jet aircraft are frequently exposed to low operating temperatures, operational problems such as filter plugging, pumpability, and related freezing-point phenomena may occur if the fuel should crystallize. In conjunction with continuing studies at NRL [1-3] on the effect of composition on the freezing point of jet fuels, one phase of the work has been concerned with model hydrocarbon fuels [1]. NRL work and that of others [4,5] have demonstrated the importance of the role of the higher n-alkanes and their interactions on the freezing points of hydrocarbon mixtures. The object of the study reported here was to delineate more clearly the interactions among the higher n-alkanes in their influence on freezing points of model hydrocarbon fuel mixtures. In an attempt to extract the most information from a set of experimental observations, it was decided to conduct a series of statistically designed experiments.

## STATISTICALLY DESIGNED MIXTURE EXPERIMENTS

For certain types of mixtures it is difficult to apply standard statistical experiments because of mixture constraints. Many products (such as gasolines, alloys, and paints) are manufactured by mixing two or more components together. In experiments with such mixtures, the observed response is usually a function only of the proportions of components and not of the total amount of the mixture. Examples of such properties are octane rating of gasoline, tensile strength of an alloy, or freezing point of a hydrocarbon mixture.

In the mixture of  $k$  components, the proportions  $x_1, x_2, \dots, x_k$  of the components (where  $x$  is mole fraction, weight fraction, etc.) must satisfy two constraints:

$$0 \leq x_i \leq 1$$

and

$$\sum_{i=1}^k x_i = 1.$$

Because of these two constraints on the components, standard statistical experimental designs are of limited use. Hence specialized mixture designs have been developed especially for this purpose [6-9]. These were based on the pioneering work of Scheffe [6], who developed the "simplex lattice" topological-geometric model for the design of mixture experiments. A commonly used design for estimating a quadratic model [8] contains experimental runs corresponding to the following points:

Type A — "pure blends" (single variable component),

Type B — "50:50 blends" (two variable components),

Type C — "check points" ("interior points"),

Type D — "equal blends" ("centroid") — equal concentrations of each component.

Manuscript approved March 7, 1983.

The application of this design to the freezing-point experiments is illustrated in Tables 1 and 2 and will be discussed later.

## EXPERIMENTAL PROCEDURE

### Hydrocarbons

Seven n-alkanes (C-10 to C-16) and a "base solution" were the components of the mixtures which were studied. Each mixture contained one or more of the n-alkanes in the base solution. The base solution consisted of 50 mol-% Isopar-M kerosene, and 25 mol-% each of t-butyl benzene and decalin. This mixture simulated jet fuel, which can have up to 25 vol-% aromatics and usually contains isoparaffins and naphthalenes as well as n-alkanes [10]. The Isopar-M kerosene consists of a relatively-high-boiling, low-freezing, narrow-cut isoparaffinic solvent whose average molecular weight is 191 [11]. The decalin (decahydronaphthalene) was found to consist of 62.7% (w/w) of the trans isomer and 37.3 wt-% of the cis isomer by gas chromatography. The other hydrocarbons used were 99 mol-% pure grade.

### Determination of Freezing Point

Freezing points were determined by ASTM method D 2386 for aviation fuels [12] with some modifications. Temperatures were read by means of a thermocouple (type "J") and potentiometer-recorder, and liquid nitrogen was used as the refrigerant. The mixtures were stirred mechanically. "Freezing point" as applied to jet fuels and similar mixtures is actually a "melting point," since in the ASTM determination it is the temperature at which the crystals (which had formed on cooling) just disappear when the temperature of the fuel is allowed to rise. However, the two phenomena take place at almost equivalent temperatures, and "freezing point" will be used here because of its wide use in the fuel literature. Furthermore the use of melting point avoids the problem of supercooling associated with freezing point. The repeatability of the ASTM freezing point method is  $\pm 0.7^\circ\text{C}$  [12].

## EXPERIMENT I

### Composition and Freezing Point

The initial experiment involved mixtures of the six n-alkanes C-10 through C-15, with C-16 and the base solution held constant at 2 mol-% and 80 mol-% respectively. The total mole-percent of the six n-alkanes comprised the remaining 18 mol-%. This experiment was based on the quadratic model design that was described in the second section, but with the range 0 to 100 mol-% transformed to the range 0 to 18 mol-%. The composition of the solutions is shown in Table 1a. The experimental runs were conducted in randomized order to assure statistically unbiased results. The observed freezing points are shown in the table.

### Preliminary Observations

Certain patterns were evident in the table prior to any statistical analysis. For the type A solutions the solution containing C-15 and C-14 gave the highest freezing points, 258.9 K and 254.7 K respectively. The effect due to C-15 and C-14 is also seen in the type B and type C solutions. Somewhat surprising, however, is the negative effect of C-13 of freezing point which can be observed in type A, B, and C mixtures. When C-13 was a component of the solution, minimum freezing points were observed, such as 239.8 K in the type A series.



Table 1a — Compositions and Freezing Points (Experiment I)

Run	Hydrocarbon Concentrations (mol-%)*						Freezing Point (K)	
	C-10	C-11	C-12	C-13	C-14	C-15	Exper.	Calc. †
Type A — Pure Blends								
26	18	—	—	—	—	—	247.4	247.2
18	—	18	—	—	—	—	247.0	246.8
28	—	—	18	—	—	—	244.1	243.7
29	—	—	—	18	—	—	239.8	238.4
6	—	—	—	—	18	—	254.7	255.5
20	—	—	—	—	—	18	258.9	258.8
Type B — 50:50 Blends								
9	9	9	—	—	—	—	247.7	247.0
14	9	—	9	—	—	—	246.7	245.4
22	9	—	—	9	—	—	244.0	242.8
12	9	—	—	—	9	—	246.0	244.6
16	9	—	—	—	—	9	252.5	253.0
24	—	9	9	—	—	—	245.6	245.2
14	—	9	—	9	—	—	242.5	242.6
36	—	9	—	—	9	—	245.7	244.7
8	—	9	—	—	—	9	252.8	252.8
35	—	—	9	9	—	—	240.3	241.0
23	—	—	9	—	9	—	247.2	246.2
25	—	—	9	—	—	9	251.0	251.2
19	—	—	—	9	9	—	245.4	243.6
31	—	—	—	9	—	9	250.8	248.6
5	—	—	—	—	9	9	253.6	252.5
Type C — Check Points								
21	10.5	1.5	1.5	1.5	1.5	1.5	245.2	246.0
27	10.5	1.5	1.5	1.5	1.5	1.5	245.3	246.0
15	1.5	10.5	1.5	1.5	1.5	1.5	245.5	245.8
30	1.5	10.5	1.5	1.5	1.5	1.5	246.9	245.8
7	1.5	1.5	10.5	1.5	1.5	1.5	245.1	244.8
17	1.5	1.5	10.5	1.5	1.5	1.5	245.0	244.8
3	1.5	1.5	1.5	10.5	1.5	1.5	240.0	242.2
13	1.5	1.5	1.5	10.5	1.5	1.5	240.1	242.2
10	1.5	1.5	1.5	1.5	10.5	1.5	246.4	247.2
33	1.5	1.5	1.5	1.5	10.5	1.5	246.4	247.2
1	1.5	1.5	1.5	1.5	1.5	10.5	252.2	252.1
34	1.5	1.5	1.5	1.5	1.5	10.5	252.3	252.1
Type D — Equal Blends								
2	3	3	3	3	3	3	243.5	245.7
4	3	3	3	3	3	3	243.2	245.7
32	3	3	3	3	3	3	243.9	245.7

\*Each solution also contained 2 mol-% C-16 and 80 mol-% base solution.

†Calculated from the following regression equation, based on the experimentally observed data:

$$\text{freezing point (K)} = 1373.3X_{10} + 1371.2X_{11} + 1353.7X_{12} + 1324.5X_{13} + 1419.7X_{14} + 1437.7X_{15} \\ - 829.7X_{10}X_{14} - 799.7X_{11}X_{14} - 425.6X_{12}X_{14} - 417.1X_{13}X_{14} - 573.2X_{14}X_{15}, \quad (1)$$

where  $X_{10}$ , for example, is the concentration of C-10 in mole-percent. The average deviation of the calculated values relative to the experimental values is  $\pm 0.9^\circ\text{C}$ .

Table 1b — Relative Strengths of the Components in Affecting the Freezing Point (Experiment I)

Relative Strength	Component	Statistical Test*	Effect
1	C-15	0.0001	Positive
2	C-13	0.0001	Negative
3	C-12	0.0052	Negative
4	C-14	0.0228	Positive
5	C-11	0.3360	Not significant
6	C-10	0.4898	Not significant

\*The probability of getting the measured freezing-point values if this component had no effect.

### Regression Equation

A regression equation based on the experimentally observed data was developed for estimating the freezing point of these mixtures and is presented in a footnote to the table. Freezing-point data calculated using this equation are shown in the table along with the experimental data for comparison. The agreement between the experimental and calculated data is good, with the average deviation being about  $\pm 1^\circ\text{C}$ .

### Relative Strengths of the n-Alkanes

Statistical tests were conducted for each of the six variable n-alkanes by comparing its estimated effect on the freezing point against a measure of random (experimental) error obtained from the experiment. The results of these statistical tests are presented in Table 1b in the order of the relative strength of the estimated effect of the n-alkane on the freezing point. As can be seen, both C-10 and C-11 have negligible effects, judged to be statistically insignificant (high values of probability) when compared with experimental error. The other four n-alkanes have strong effects (low values of probability), with C-12 and C-13 exhibiting negative effects (an increase in concentration of these n-alkanes being predicted to lower the freezing point) and with C-14 and C-15 having positive effects. As was mentioned, it was observed that C-13 has a stronger negative effect than C-12.

In addition to these main effects, there were statistically significant interaction effects. Each of the other alkanes C-10, C-11, C-12, C-13, and C-15 interacted with C-14. This means that the effect that C-10, C-11, C-12, C-13, and C-15 each has on freezing point depends on the C-14 concentration. Equivalently the effect that a change in C-14 concentration has on the freezing point depends on the concentrations of C-10, C-11, C-12, C-13, and C-15. Although these secondary effects were statistically significant, they were generally minor.

## EXPERIMENT II

As a result of the interesting observations in experiment I (with C-16 constant at 2 mol-%), a second experiment was defined in order to determine the effects of varying the concentration of C-16 and the base solution. In addition, because of the statistically insignificant effects of C-10 and C-11, these two n-alkanes were omitted in further experiments.

### Composition and Freezing Point

In the second experiment the concentrations of each of the n-alkanes C-12 through C-16 varied from 0 to 30 mol-%, with the concentration of the base solution being varied over the range 70 to 100 mol-%. A quadratic-model mixture design was again used after the necessary transformations of ranges were made. The compositions of the experiment II solutions are shown in Table 2a along with experimental freezing points.

### Preliminary Observations

Examination of Table 2a prior to any statistical analysis reveals the expected increase of freezing point with increasing carbon number. In the case of the type A solutions the freezing point goes from 246.8 K (30 mol-% C-12) up to 276 K (30 mol-% C-16). Similar trends can be observed for the type B and type C mixtures. The positive freezing-point effect of each of the n-alkanes is easily seen when its data are compared to those of solutions containing no n-alkanes, such as the base solution (run 7) in the type A series. The freezing point for the run 7 solution was actually too low to be measured by the ASTM procedure, and the run was discontinued around 142 K. The freezing points of mixtures containing C-13 did not show the unusual negative effects found in experiment I, and no minima were

Table 2a — Compositions and Freezing Points (Experiment II)

Run	Hydrocarbon Concentrations (mol-%)						Freezing Point (K)	
	C-12	C-13	C-14	C-15	C-16	Base Soln.	Exper.	Calc.*
Type A								
10	30	—	—	—	—	70	246.8	247.9
22	—	30	—	—	—	70	249.6	249.7
24	—	—	30	—	—	70	264.0	258.8
28	—	—	—	30	—	70	265.4	261.6
9	—	—	—	—	30	70	276.0	279.0
7	—	—	—	—	—	100	164-169†	252.4
Type B								
2	15	15	—	—	—	70	242.2	239.8
1	15	—	15	—	—	70	253.8	253.3
29	15	—	—	15	—	70	256.0	254.7
5	15	—	—	—	15	70	268.6	263.4
17	15	—	—	—	—	85	238.7	236.1
14	—	15	15	—	—	70	255.0	254.3
8	—	15	—	15	—	70	253.6	255.7
15	—	15	—	—	15	70	268.2	264.3
30	—	15	—	—	—	85	240.2	238.1
21	—	—	15	15	—	70	259.3	260.2
18	—	—	15	—	15	70	267.6	268.9
19	—	—	15	—	—	85	255.2	255.6
11	—	—	—	15	15	70	268.2	270.3
25	—	—	—	15	—	85	257.5	257.0
3	—	—	—	—	15	85	268.6	265.7
Type C								
12	17.5	2.5	2.5	2.5	2.5	72.5	243.0	248.2
6	2.5	17.5	2.5	2.5	2.5	72.5	247.0	249.3
27	2.5	2.5	17.5	2.5	2.5	72.5	253.0	257.5
20	2.5	2.5	2.5	17.5	2.5	72.5	259.0	258.9
4	2.5	2.5	2.5	2.5	17.5	72.5	269.4	267.6
26	2.5	2.5	2.5	2.5	2.5	87.5	246.7	249.8
Type D								
23	5	5	5	5	5	75	251.9	254.2
16	5	5	5	5	5	75	251.6	254.2
13	5	5	5	5	5	75	251.6	254.2

\*Calculated from the following regression equation, based on the experimentally observed data:  
 freezing point (K) =  $672.7X_{12} + 645.7X_{13} + 273.7X_{14} + 283.0X_{15} + 340.9X_{16}$   
 $+ 252.3X_B - 401.0X_{12}X_{13} - 622X_{12}X_B - 574.6X_{13}X_B$  (2)

where  $X_{12}$ , for example, is the concentration of C-12 and  $X_B$  is the concentration of the base solution. The average deviation is  $\pm 2.3^\circ\text{C}$ .

†The base solution did not form crystals on cooling but formed a glassy "solid" at about 164 K and re-liquified around 169 K. The run was discontinued at 142.0 K.

Table 2b — Relative Strengths of the Components in Affecting the Freezing Point (Experiment II)

Relative Strength	Component	Statistical Test*	Effect
1	C-16	0.0001	Positive
2	Base solution	0.0001	Negative
3	C-12	0.0007	Negative
4	C-13	0.0009	Negative
5	C-15	0.0142	Positive
6	C-14	0.1163	Positive (borderline)

\*The probability of getting the freezing-point values measured if this component had no effect.

observed for solutions containing this alkane. The differences in behavior of C-13 in experiment I and in experiment II seem to be related to the C-16 concentration, which was held at 2 mol % in all solutions of experiment I, whereas the solutions of experiment II had varying C-16 concentrations, including solutions with C-16 absent.

### Regression Equation

The regression equation developed for estimating freezing points for the experiment II mixtures is shown in Table 3. Calculated data are also shown in the table. The calculated data for experiment II did not match the experimental data as well as they did for experiment I. This is to be expected, because a wider range of concentrations was examined. The average deviation for experiment II was about  $\pm 2^\circ\text{C}$ .

### Relative Strengths of the n-Alkanes

Results of the statistical test of the effects on freezing point are shown in Table 2b. It is seen that C-14, C-15, and C-16 had positive effects on the freezing point and that C-12, C-13, and the base solution had negative effects. Although the positive contributions were as expected, with C-16 having the strongest effect followed by C-15 and C-14, the negative contributions cannot be given a straightforward interpretation, since the regression equation in Table 2a indicates a strong interaction between the three negative components (C-12, C-13, and the base solution). This interaction may be illustrated by considering runs 2, 10, and 22 involving only C-12 and C-13, together with 70-mol-% base solution (C-16 = 0). The solution which contained 0 mol-% C-12 and 30 mol-% C-13 (run 22) froze at 249.6 K, and the solution containing 30 mol-% C-12 and 0 mol-% C-13 (run 10) froze at 246.8 K. However, the solution containing 15 mol-% of each of these two alkanes (run 2) froze at 242.2 K, a lower temperature than for the other two. This lowering was also obtained for the calculation using the regression equation.

Hence it was decided to run a third experiment to examine this effect in detail.

## EXPERIMENT III

The range of exploration in the first two experiments was set relatively wide to provide as much information as possible. The resulting statistical analysis furnished some interesting information and in turn raised some questions. The effects of C-12, C-13, and their mixtures with varying concentrations of C-16 in particular appeared to merit special attention. It was decided to conduct more extensive experiments in a limited composition region.

### Composition and Freezing Point

Experiment III consisted of five sets of experiments in which the C-16 concentration varied between 0 and 5 mol-%. Within each set, as shown in Table 3, nine combinations of C-12 and C-13 were prepared. This is based on a different type of statistical experiment, a response surface design [9]. The primary reason for the change to this type of design was that it permits a more detailed examination of C-12 and C-13 in the presence of C-16. In this experiment C-12, C-13, and C-16 were considered active variables, and the base stock was considered as a "slack" variable.

### Preliminary Observations

Again prior to any statistical analysis certain observations could be made. First, it can be seen from Table 3 and from Fig. 1 that at 5 mol-% C-16 all the freezing points were about the same (average =  $255^\circ\text{C}$ ) regardless of the concentrations of C-12 and C-13. It can also be seen from Table 3 and,

Table 3 — Compositions and Freezing Points (Experiment III)

Run	Point No.	Hydrocarbon Concentrations (mol-%)				Freezing Point (K)	
		C-12	C-13	C-16	Base Sol.	Exper.	Cal.*
1	1	0	12	0	88	238.0	235.7
2	2	6	6	0	88	229.0	230.8
3	3	12	0	0	88	234.4	233.6
4	4	0	18	0	82	241.8	243.8
5	5	9	9	0	82	232.8	233.2
6	6	18	0	0	82	239.9	239.9
7	7	6	18	0	76	244.0	242.8
8	8	12	12	0	76	237.8	237.5
9	9	18	6	0	76	239.6	239.9
10	1	0	12	1	87	234.9	234.1
11	2	6	6	1	87	229.2	231.0
12	3	12	0	1	87	235.4	234.1
13	4	0	18	1	81	241.2	241.3
14	5	9	9	1	81	234.0	233.4
15	6	18	0	1	81	238.6	239.4
16	7	6	18	1	75	241.4	241.7
17	8	12	12	1	75	237.6	237.4
18	9	18	6	1	75	239.4	239.2
19	1	0	12	1.67	86.33	236.8	237.7
20	2	6	6	1.67	86.33	242.2	239.9
21	3	12	0	1.67	86.33	244.0	243.7
22	4	0	18	1.67	80.33	240.6	240.1
23	5	9	9	1.67	80.33	235.4	238.1
24	6	18	0	1.67	80.33	238.6	239.8
25	7	6	18	1.67	74.33	240.8	240.8
26	8	12	12	1.67	74.33	237.2	236.8
27	9	18	6	1.67	74.33	235.6	234.3
28	1	0	12	3.33	84.67	250.6	250.6
29	2	6	6	3.33	84.67	251.2	251.1
30	3	12	0	3.33	84.67	250.8	250.5
31	4	0	18	3.33	78.67	244.8	244.8
32	5	9	9	3.33	78.67	248.8	249.1
33	6	18	0	3.33	78.67	250.2	250.6
34	7	6	18	3.33	72.67	242.4	242.3
35	8	12	12	3.33	72.67	246.6	246.7
36	9	18	6	3.33	72.67	250.4	250.0
37	1	0	12	5	83	255.0	255.0
38	2	6	6	5	83	255.4	255.6
39	3	12	0	5	83	256.4	256.1
40	4	0	18	5	77	254.6	254.5
41	5	9	9	5	77	255.4	255.3
42	6	18	0	5	77	255.6	256.1
43	7	6	18	5	71	254.0	254.4
44	8	12	12	5	71	255.4	255.0
45	9	18	6	5	71	255.6	255.5

\*Calculated from the following regression equations, based on the experimentally observed data

$$\text{freezing point when C-16} = 0.00 \text{ mol-\% (K)} = 231.9 - 46.3 X_{12} - 35.0 X_{13} + 506.9 (X_{12})^2 + 562.5 (X_{13})^2 \quad (3)$$

$$\text{freezing point when C-16} = 1.00 \text{ mol-\% (K)} = 230.9 - 14.0 X_{12} - 34.7 X_{13} + 340.2 (X_{12})^2 + 513.9 (X_{13})^2 \quad (4)$$

$$\text{freezing point when C-16} = 1.67 \text{ mol-\% (K)} = 244.6 + 30.3 X_2 - 122.7 X_{13} - 319 (X_{12})^2 + 542.1 (X_{13})^2 \quad (5)$$

$$\text{freezing point when C-16} = 3.33 \text{ mol-\% (K)} = 254.3 - 54.2 X_{12} + 11.3 X_{13} + 186.5 (X_{12})^2 + 355.2 (X_{13})^2 \quad (6)$$

$$\text{freezing point when C-16} = 5.00 \text{ mol-\% (K)} = 256.2 - 0.6 X_{12} - 9.4 X_{13} \quad (7)$$

The average deviation is  $\pm 0.6^\circ\text{C}$

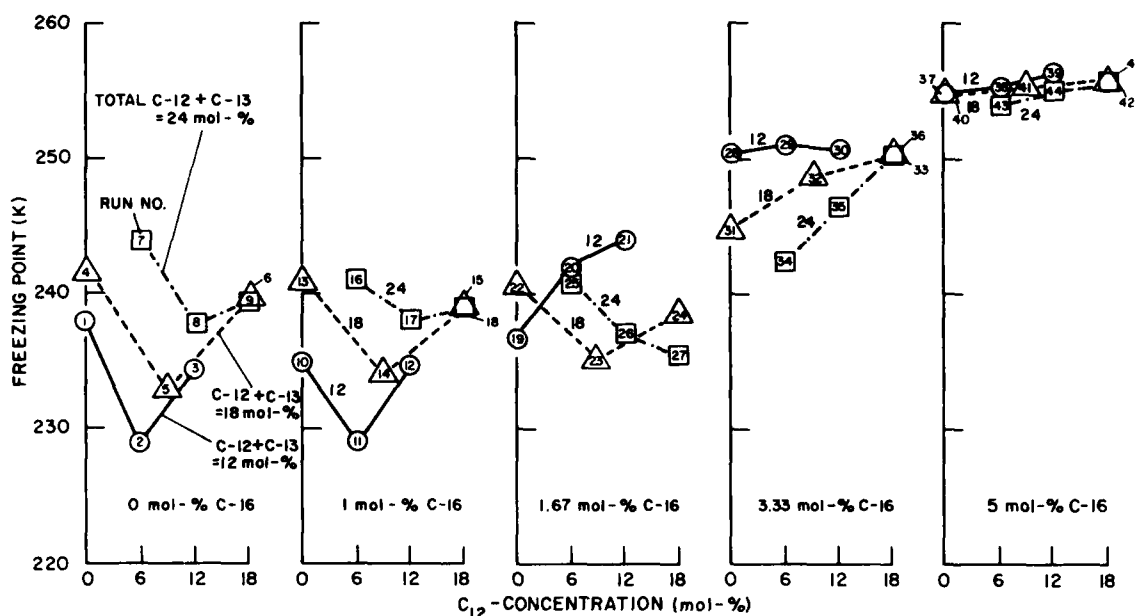


Fig. 1 — Freezing point as a function of the concentration of C-12, C-13, and C-16 mixtures (experiment III)

more readily, from Fig. 1 that at 0 and 1 mol-% C-16 equal parts of C-12 and C-13 yielded lower freezing points than either of the n-alkanes alone; that is, the freezing point was lower for run 2 than for runs 1 and 3, was lower for run 11 than for runs 10 and 12, was lower for run 5 than for runs 4 and 6, was lower for run 14 than for runs 13 and 15, etc. At 1.67 mol-% C-16 this trend continued only for run 23 in comparison with runs 22 and 24. For run 20 in comparison with runs 19 and 21 and for run 26 in comparison with runs 25 and 27 (at 1.67 mol-% C-16), and for all runs at 3.33 mol-% C-16 and above, this phenomenon did not occur.

### Regression Equations

Attempts to fit an overall regression model to the 45 observations of experiment III met with failure; no model was found to provide a reasonable fit. This indicated that something unusual was occurring in these mixtures, and this was related to the C-16 concentration. Consequently a separate regression equation was fit for each level of C-16 (Table 3). The calculated and experimental data were in good agreement, with an overall average deviation of about  $\pm 0.6^\circ\text{C}$ .

### Interaction Among C-12, C-13, and C-16

It can be seen from Fig. 1 and also from Table 5 that C-16 interacts strongly with C-12 and C-13. Furthermore, as was stated, it is difficult to make statements about the effects of C-12 and C-13 without fixing the C-16 concentration.

At the higher concentrations of 3.33 and 5 mol-% C-16 the C-16 appears to take over, so that at higher C-16 concentrations the C-12 and C-13 have little or no effect. On the other hand, at concentrations of 0 and 1 mol-% C-16 both C-12 and C-13 have strong interacting effects, and regardless of whether the total C-12 plus C-13 concentration is 12, 18, or 24 mol-%, a mixture containing both C-12 and C-13 results in lower freezing points than a mixture containing only one of these alkanes. When

the concentration of C-16 is 3.33 mol-%, C-12 and C-13 have about the same effect if their total concentration is 12 mol-%. However, as their total concentration increases to 18 mol-% and 24 mol-%, C-13 has a much stronger effect than C-12. When the concentration of C-16 is 1.67 mol-%, it appears that a transition occurs between the interaction seen at 0 mol-% C-16 and the strong C-13 effect seen at 3.33%. At a concentration of 1.67 mol-% C-16, C-12 and C-13 perform much differently, depending on whether their total concentration is 12, 18, or 24 mol-%.

## SUMMARY OF EXPERIMENTS I, II, AND III

### Relative Freezing-Point Effects

Table 4 gives the statistical freezing-point effects of each component in each of the three experiments. The "freezing-point effect" ( $E_i$ ) for each component shown in the table represents the change in the calculated freezing point of the mixture ( $\Delta T_m$ ) per unit increase in concentration ( $\Delta X_i = 1$  mol-%) for that component. The estimation of the freezing-point effect ( $E_i = \Delta T_m / \Delta X_i$ ) also requires that the concentrations of the other components be decreased accordingly so as to remain within the constraints of the experimental design.

In addition to the n-alkanes and base solution, which are listed in the hydrocarbon column of Table 4, a row for C-12 plus C-13 has been added, since their combined effect has been shown to be important. In the case of C-12 plus C-13 the interaction effect ( $E_i$ ) represents the portion of the freezing-point effect resulting from increasing C-12 and C-13 that is not accounted for by increasing them separately. For example, if  $E_{12,13}$  is the effect of increasing the concentrations of C-12 plus C-13 ( $X_{12} + X_{13}$ ),  $E_{12}$  is the effect of increasing only  $X_{12}$ , and  $E_{13}$  is the effect of increasing only  $X_{13}$  (each increase being 1 mol-%), then the interaction effect is

$$E_i = E_{12,13} - E_{12} - E_{13}.$$

The last row in Table 4, for C-12 plus C-13, was estimated using this equation.

Table 4 — Relative Freezing-Point Effects of Hydrocarbons

Hydrocarbon	Effect on Freezing Point (°C/mol)						
	Experiment I	Experiment II	Experiment III				
	C-16 = 2 mol-%	C-16 variable	C-16 = 0 mol-%	C-16 = 1 mol-%	C-16 = 1.67 mol-%	C-16 = 3.33 mol-%	C-16 = 5 mol-%
C-10	+0.100	—	—	—	—	—	—
C-11	+0.073	—	—	—	—	—	—
C-12	-0.133	-0.252	+0.183	+0.230	-0.164	+0.067	+0.047
C-13	-0.487	-0.180	+0.507	+0.402	-0.069	-0.454	-0.091
C-14	+0.653	+0.184	—	—	—	—	—
C-15	+0.873	+0.296	—	—	—	—	—
C-16	—	+0.992	—	—	—	—	—
Base soln.	—	-0.072	—	—	—	—	—
C-12 plus C-13	-0.144	-0.547	-0.161	-0.128	-0.034	+0.025	-0.006

The relative freezing-point effects for all three experiments, which are shown in Table 4, may be summarized as follows:

- C-16, C-15, and C-14 have strong positive effects (in that order);
- C-12 and C-13 have strong effects;

- The combined effect of C-12 plus C-13 is greater than that of either alkane;
- The individual effects of C-12 and C-13, as well as the interaction between them, are strongly influenced by the presence of C-16;
- C-10 and C-11 have negligible effects.

#### Predicted Minimum and Maximum Freezing Points

The data in Table 5 show predicted minimum and maximum freezing points as a function of composition. These data were calculated by means of the regression equations using the Kuhn-Tucker conditions [13] of nonlinear programming. Because of the constraints on the concentrations in the experimental design, standard methods of calculus cannot be used to obtain predicted minima and maxima.

Table 5 — Minimum and Maximum Freezing Points as Predicted by Regression Equations (1) through (7)

Experiment	C-16 Concentration (mol-%)	Predicted Freezing Point (K)	Calculated Component Concentrations at the Predicted Freezing Point (mol-%)						
			C-10 and C-11	C-12	C-13	C-14	C-15	C-16	Base Soln.
Minimum Freezing Point									
I	2	238.4	0	0	18.0	0	0	2.0*	80.0*
II	variable	233.9	—	11.0	8.2	0	0	0	80.8
III	0	230.7	—	6.8	5.2	—	—	0*	88.0
	1	231.0	—	6.0	6.0	—	—	1.0*	87.0
	1.67	234.3	—	18.0	6.0	—	—	1.67*	74.33
	3.33	242.3	—	6.0	18.0	—	—	3.33*	72.67
	5	254.4	—	6.0	18.0	—	—	5.0*	71.0
Maximum Freezing Point									
I	2	258.8	0	0	0	0	18.0	2.0*	80.0*
II	variable	279.0	—	0	0	0	0	30.0	79.0
III	0	243.8	—	0	18.0	—	—	0*	82.0
	1	241.7	—	6.0	18.0	—	—	1*	75.0
	1.67	243.6	—	12.0	0	—	—	1.67*	86.33
	3.33	251.1	—	5.9	6.1	—	—	3.33*	84.67
	5	256.1	—	12.0	0	—	—	5.0*	83.0

\*Fixed concentration.

It is seen that the mixture giving the lowest predicted freezing point (230.7 K) contained only C-12 (6.8 mol-%), C-13 (5.2 mol-%), and the base solution (88.0 mol-%). In experiments II and III all minimum-freezing-point mixtures had both C-12 and C-13 present. In Experiment I the minimum-freezing-point mixture was with 18.0 mol-% C-13.

The maximum-freezing-point mixture (279.0 K) contained 30 mol-% C-16. In all cases the maximum freezing points occurred for mixtures containing C-15 plus C-16 or C-16 except the first series of experiment III (0 mol-% C-16), where no C-16 was included in any of the mixtures studied.

The data for the minimum and maximum freezing points are all in accordance with the values of the relative freezing-point effect previously discussed.



## SUMMARY AND CONCLUSIONS

As part of continuing studies at NRL on the effect of composition on the freezing point of model hydrocarbon fuels, a series of statistically designed experiments were run in order to extract the maximum amount of information from a limited number of experiments. Three series of experiments were run, and in each case regression equations were developed to describe the effect of composition on different mixtures of higher n-alkanes and other hydrocarbons.

As a result of these studies it has been shown that the n-alkanes and the interactions among them play an important part in freezing point. It was shown that C-16, C-15, and C-14 (in that order) have strong positive effects. Although C-12 and C-13 have strong effects in the mixtures which were studied, these effects are significantly influenced by the amount of C-16 present. C-12 and C-13 in combination interacted with each other and showed stronger negative effects than either of the individual n-alkanes, but this interaction was found to be greatly dependent on the presence of C-16. This behavior was consistent with the changes or reversals of slope in Van't Hoff plots of freezing point versus C-13 concentration at varying concentrations of C-16 which were reported in earlier NRL work [1]. C-10 and C-11 were found to have negligible negative effects on freezing point.

## ACKNOWLEDGMENT

The authors express their appreciation to Mr. John DeGuzman for determining many of the freezing points in these experiments.

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